



Determination of Sulfur Content of Automotive Fuels – Ultraviolet Fluorescence Method According to EN ISO 20846 – Removal of Nitrogen Interferences by N-based Cetane Improvers

Introduction

During the production of motor fuels by hydration of coal or vegetable oil, as well as during the production of traditional fuels based on mineral oil with biodiesel addition, end products with affected ignition characteristics can occur. In this case special additives – generally known as cetane improver – are used to enhance the ignitability (cetane number). Nitrogen compounds have proven to be especially suitable and cost efficient, such as amyl nitrate, cyclohexyl nitrite, triethylene glycol dinitrate, or 2-ethylhexyl nitrate (2-EHN). Besides the positive effect on the ignition characteristics these substances also lead to increased nitrogen content in the final product. This is a serious problem because the nitrogen can lead to false positive results when determining the TS content in fuels. Considering the fact that many fuels classified as sulfur-free already have an actual TS content close to the statutory limit value of 10 ppm (ASTM D4814, D6751//DIN EN 590, DIN EN 14214), the sulfur content determined can exceed the specified threshold easily, if nitrogen-containing cetane improvers are used. The fuel no longer complies with the requirements and a costly post-treatment is needed. However, this effort can be avoided when using a matrix-independent UV detection technique that makes it possible to differentiate between sulfur and the nitrogen interference.

Challenge

Avoiding the exceedance of given legal limits for total sulfur (TS) impurities in fuels caused by the positive cross sensitivity of NO to the UV-fluorescence technique.

Solution

Elimination of the interfering N-compounds by cold plasma ionization (MPO technology).

The Micro Plasm Optimization (MPO), a patented technique developed as an enhancement of the classic UV-fluorescence, guarantees reliable results within a short measurement time. It converts the interfering NO molecules to harmless species. There is no need for additional auxiliary materials (e.g., catalysts), multiple injections, or matrix separation by trap-and-release approaches.

Materials and Methods

Samples and Reagents

Different fuel samples with and without N-containing additives as well as S and N standard solutions have been analyzed.

Sample Preparation

The samples were analyzed directly. No sample preparation was required.

Calibration

Liquid calibration standards based on dibenzothiophene (S) in isooctane were used to calibrate the analysis system in the appropriate concentration range. Matrix-related calibration strategies are not required since the combustion is optimized and interfering components are eliminated before detection.

Instrumentation

The fuel samples have been analyzed on a compEAct S^{MPO} elemental analyzer, equipped with HiPerSens UVFD detection system and an autosampler LS 2 for fully automated sample introduction.

The HiPerSens UVFD includes the patented MPO, which ensures the correct sulfur analysis even in the presence of elevated nitrogen contents. The MPO fully automatically renders interfering nitrogen compounds harmless as an integral step of the analysis process. For all samples a volume of 10 µL was injected directly into the combustion tube. The quantitative combustion took place at 1050° C.

To ensure that this process is fast and completely matrix-independent, a specially designed quartz glass reactor including a quartz pyrolyzer was used. The sophisticated management of process gases allows lighter sample components to evaporate quickly and safely in a pure inert carrier gas atmosphere. Heavier components are pyrolyzed quickly and controlled on the active surface of the quartz pyrolyzer. This way only the gaseous components enter the combustion zone in the first stage of the process. In the second stage, the formed pyrolysis products as well as other heavier sample components, which were retained by the quartz pyrolyzer, are digested quantitatively in the presence of pure oxygen.

Before entering the MPO, the combustion gases are cleaned and dried. Afterwards, all interfering nitrogen compounds are removed by the powerful cold plasm ionization. The remaining SO₂ is detected by means of UV fluorescence.

Method Parameters

Standard method settings for vertical operation provided in the method library are applied. The parameter settings for the combustion process are summarized in Table 1. The evaluation parameters for the detection of sulfur are given in Table 2.

Table 1: Process parameters

| Parameter | Specification |
|------------------------------------|---------------|
| Furnace temperature | 1050 °C |
| Second combustion | 60 s |
| Ar flow (first phase) | 100 mL/min |
| O ₂ main flow | 200 mL/min |
| O ₂ flow (second phase) | 100 mL/min |
| Draw up | 2 µL/s |
| Injection | 0.5 µL/s |

Table 2: S detection parameters

| Parameter | Specification |
|-----------------------|---------------|
| Max. integration time | 300 s |
| Start | 0.1 ppb |
| Threshold | 0.11 ppb |
| Stability | 7 |

Results and Discussion

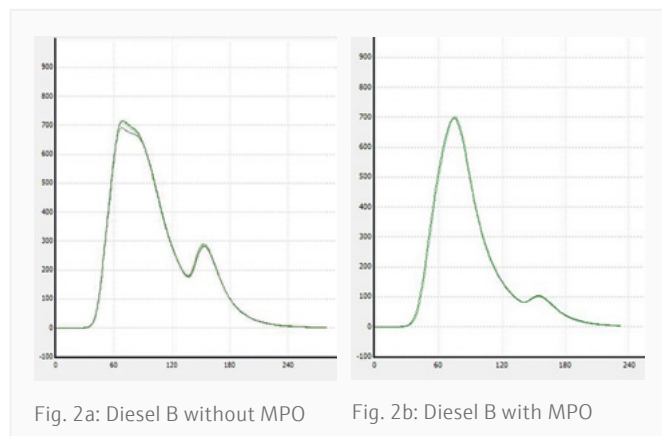
The results of the two diesel fuel samples and the standards summarized in Table 3 show the averages of three replicate measurements. Due to the matrix-optimized combustion a threefold determination is sufficient to achieve results within 3 % RSD. This remarkably affects the sample processing time and allows a higher sample throughput. The analysis results received and their reproducibility prove the quality of the digestion process. The overall performance of the analysis system was validated by analyzing a TS standard material with known concentration, results are given in Table 3.

Table 3: Results of the sulfur determination with and without utilization of MPO technique

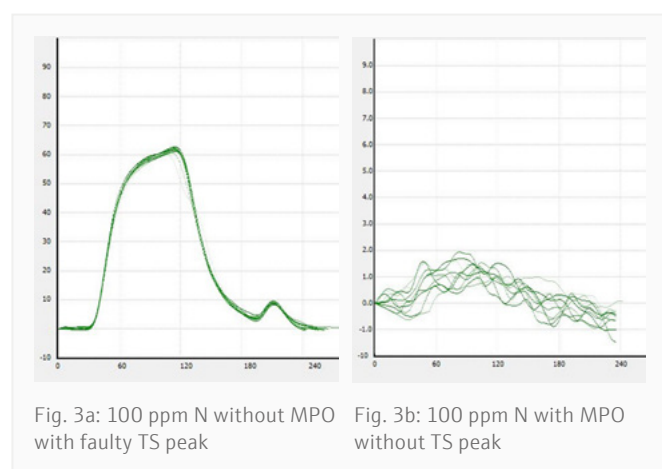
| Measurement | TS ± RSD with MPO | TS ± RSD without MPO | TN * |
|---------------------|----------------------|-------------------------|----------|
| Diesel A | 6.2 ppm ± 1.12 % | 6.7 ppm ± 2.06 % | 26 ppm |
| Diesel B | 9.8 ppm ± 1.17 % | 10.6 ppm ± 0.22 % | 75 ppm |
| FAM Normal Gasoline | 93.8 ppb ± 7.91% | 94.1 ppb ± 7.82% | 363 ppb |
| Gasoline | 969 ppb ± 2.17% | 973 ppb ± 2.69% | 1.60 ppm |
| Standard 5 ppm S | 5.03 ppm ± 2.38 % | 4.99 ppm ± 1.23 % | n. a. |
| Standard 100 ppm N | 0.02 ppm ± 4.55 % | 1.03 ppm ± 1.67 % | 100 ppm |

* TN content determined by means of elemental analysis (CLD)

Typical measuring curves for the two applied techniques for sample "Diesel B" and the "Standard 100 ppm N" solution are shown in Figures 2a–b and 3a–b.



The highly sensitive detector enables injection of smallest volumes and thus fast analysis results in approximately 3 minutes, independent of the analyzed sample or the sulfur content.



The analysis curves of the sulfur-free 100 ppm N standard prove the effectiveness of the MPO technique as a valuable tool to eliminate the interfering NO completely before analyzing the TS content.

Conclusion

The compEAct S^{MPO} facilitates fast and interference-free determination of sulfur contents in the presence of nitrogen-containing additives. Especially designed for fuel applications, it enables reliable analysis of challenging matrices and simplifies routine work.

The wide liner operation range of the HiPerSens detector makes sample pretreatment, e.g., dilution of higher concentrated samples or enrichment of ultratraces by trap-and-release technique a thing of the past. It thus reduces the risk of operator errors and remarkably shortens the processing time of each sample independent of the concentration.

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